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25 YEAR RE-REVIEW

FORMALDEHYDE CHEMISTRY

REVIEW OF RUSSIAN TECHNOLOGY

The following review of Russian formaldehyde chemistry is based principally on English and German abstracts of Russian articles. A few papers, which appeared outstanding, were studied in the original Russian by the writer. The German translation of Orlov's book was used in covering early studies. Y. Mayor's review of the literature on formaldehyde manufacture (34) also served as a valuable source of information on Russian work prior to 1939.

I. HISTORY

Formaldehyde was first prepared by A. M. Butlerov in 1859 (8) in a study of compounds derived from methylene iodide. Although he did not characterize the new product as formaldehyde, he published an accurate description of formaldehyde and its polymers as well as an account of their simple chemical properties including the production of hexamethylene tetramine by reaction with ammonia. He regarded these compounds as derivatives of "oxymethylene" but noted that his solid "oxymethylene" polymer behaved like the unknown "formyl aldehyde". The true nature of formaldehyde was established in 1868 by the German chemist, Hofmann, who demonstrated its synthesis from methanol by oxidation over a platinum catalyst.

The first book on formaldehyde was written by E. I. Orlov in Russia in 1908. A German translation of this book by Carl Kietabl (45) was published in 1909 ("Formaldehyde, J.E.Orloff, Verlag Von Johann Abrosius Barth, Leipzig, 1909").

II. PRODUCTION OF FORMALDEHYDE

A. Methanol Process

Kablukov (15) reported the use of platinized asbestos as a catalyst for the preparation of formaldehyde from methanol and air in 1882. This was a simple replacement for the platinum wire employed by Hofmann. In 1907-8, E.I.Orlov (45,46), made a detailed study of the process as previously developed by German and French investigators. He measured the effect of variations in the ratio of methanol to air in the feed gases, the velocity of the gas current, the nature and dimensions of the catalyst mass and the purity of the methyl alcohol employed. He obtained his best results (approx. 55% yields) with the copper gauze catalyst as compared with platinum, vanadium oxide and iron. This work was used a few years later by the German firm of F.H.Meyer in the construction of an improved formaldehyde unit. Further research on the manufacturing process by Methodie Ivanovich Kuznezov (29) corroborated German findings on the superiority of silver catalyst. In 1913, the silver gauze catalyst was introduced in United States operations with Kuznezov's patent (30). Additional processing details and reaction mechanism studies by Gurewitsch and Tschirwinskaja (14) in 1935 duplicated the approximately 90% yields reported by Thomas in America in 1925. However, the Russian investigators concluded that the process mechanism involved direct oxidation of methanol as well as dehydrogenation followed by combustion of the hydrogen liberated by this reaction. This is still a moot question.

B. Hydrocarbon Oxidation

Russian research on hydrocarbon oxidation processes for formaldehyde appears to have been centered on methods employing methane or natural gas as raw materials.

Early English, French, and American investigators demonstrated the formation of low yields of formaldehyde by the partial oxidation of methane around 1900. However, the gaseous products from these procedures contained only small concentrations of formaldehyde. Also, the problem of scrubbing these gases and concentrating the dilute solutions obtained did not appear practical from a commercial standpoint. This still seems to be the case and we have no authentic knowledge of the successful operation of a commercial process based on oxidation of methane or a natural gas consisting predominantly of this hydrocarbon. However, Y. Mayor in a French review article (34 -- L'Industrie Chimique, 26, 291-2 (1939)) states that the Russians have obtained a 70% yield of formaldehyde based on methane and that the use of this process has resulted in a 50% reduction in the price of formaldehyde. No evidence is given for this statement.

S.S.Medvedev and co-workers published results of thorough studies of methane oxidation in the years 1924 - 1932 (35,36,37,38). A large number of solid as well as gaseous catalysts were investigated. Medvedev's best results (approx. 5% conversions) appear to have been obtained with phosphate and borate catalysts (36) using small concentrations of gaseous hydrogen chloride as a promoter (38). Since 1932 Medvedev has been working on problems of hydrocarbon polymerization. Our most recent reference is dated 1951 and deals with styrene. Most of Medvedev's papers have appeared in the Transactions of the L. Ya. Karpov Phys. Chem. Institute. In 1934, Tichomorowa (58) studied vanadium pentoxide as a catalyst for the methane oxidation. Kreshkov (23) studied vanadium trioxide, cuprous chloride and barium chloride supported on coke using a gaseous mixture of methane containing chlorine and water vapor. Kreshkov's yields averaged about 1%. Kushnerev

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and Shekter (27) used atomic oxygen and passed the gases through a discharge tube. A study of the simultaneous oxidation of methane, carbon monoxide and hydrogen by Sakharov and Durynina in 1948 does not indicate appreciable formation of formaldehyde (53).

Khorzhev's study (see Sect. III) of the properties of formaldehyde solution in 1935 (20, 22) was carried out in connection with research on the development of Medvedev's process for the oxidation of natural gas. The main objective was to discover a practical method for concentrating the dilute formaldehyde contaminated with hydrogen chloride. A Russian patent (21) covering concentrating formaldehyde by adding calcium chloride and distilling at atmospheric pressure resulted from this work. Khorzhev (20) states that this research took place at Soyuz and paraformaldehyde from the Kuskovsk Formaldehyde Plant was used to prepare the solutions for the experiments. The Kuskovsk Plant probably employed a methanol process.

III. PHYSICAL PROPERTIES OF FORMALDEHYDE

Morozov and co-workers (40) have recently calculated force constants for the formaldehyde molecule from the vibrational spectra of CH_2O and CD_2O.

As previously noted, Khorzhev and Rossinskaya (20) made a thorough study of the properties of formaldehyde solution in 1935. They were apparently the first investigators to use an equilibrium still for determining the partial pressure of boiling formaldehyde solutions. Although this type of instrument tends to give somewhat high partial pressure values, their work represented an important contribution to the understanding of the peculiar problems of formaldehyde distillation. No references have been found to Khorzhev's work since 1935. Rossinskaya and Leites reported some work on sodium nucleinate in 1948 and Frolova, who worked with Khorzhev

and Rossinskaya on the problem of concentrating formaldehyde, reported studies
with Ravich on the phenol-formaldehyde reaction in 1953.

IV. CHEMICAL PROPERTIES OF FORMALDEHYDE

Kuznetzov (29) studied the stability of formaldehyde gas over hot copper in
1913 in connection with his work on the development of a manufacturing process.
Medvedev and Robinson (38) measured the rate of decomposition at various temperatures
in a refractory glass tube at 450° to 700°C. The reaction of the free hydroxyl group
with formaldehyde in the gas phase oxidation reaction has been studied by Avramenko
and Lorentso (3).

With regard to reactions of formaldehyde with formaldehyde, W. Tischenko's
work on the production of methyl formate by the reaction which now bears his name is well
known (62). Balezin (4) studied the formation of sugars by the aldol-type condensation
of aqueous formaldehyde in 1947 and concluded that calcium oxide did not act merely
as a base in catalyzing this reaction but was an essential component of an intermediate
complex.

A. Reactions with Inorganic Agents

V.E.Tischenko and co-workers (63, 64) prepared dibromo- and di-iodomethyl
ethers by reaction of polyoxymethylene with the corresponding hydrogen halides.
The bromo ether was also made by the reaction of phosphorus, bromine water and
polyoxymethylene.

In 1948-1949, T.I.Kunin (24, 25) reported a detailed study of the mechanism
of the decomposition of sodium formaldehyde sulfoxylate which is employed as a
reducing agent for stripping and discharging dyed textiles.

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B. Reactions with Alcohols

Lyubomilov and Terentyev (32) report the preparation of 2-ethyl propenol by reacting formaldehyde with a butanol solution of sodium butylate. On reduction of this product, 2-methylbutanol was obtained as would be expected. The primary condensation has no analogs in known formaldehyde chemistry but the work seems genuine.

The higher aliphatic chloromethyl ethers have been prepared and characterized by Kursanov and Setkina (26) from formaldehyde, hydrogen chloride and the various alcohols using routine preparative techniques.

C. Reactions with Aldehydes and Ketones

Considerable apparently competent research has been carried out on the condensation of formaldehyde with acetaldehyde and ketones to give polyhydroxy compounds. These materials are important as intermediates for alkyd resins and explosives such as PETN.

Stepanov and Shchukina (57) studied the mechanism of the reaction of formaldehyde and acetaldehyde to produce pentaerythritol. They successfully demonstrated the presence of beta-hydroxypropionaldehyde ($HOCH_2CH_2CHO$) as a reaction intermediate. Kuzin (28) discovered that small amounts of sugars (e.g. glucose) catalyze the formation of pentaerythritol.

Tilichenko and co-workers have recently made a detailed study of the condensation of formaldehyde with menthone (59), acetone (60) and cyclohexanone (61). The acetone and cyclohexanone reactions have received considerable study both here and abroad. The Russians studied the factors controlling yields of the simple hydroxy compounds and by-product resins. There is no evidence that outstanding yield improvements were obtained.

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D. Reaction with Phenols

Vansheidt and co-workers (65, 68) have studied the mechanism of the phenol-formaldehyde reaction and the production of phenol alcohols. A recent (1953) study by Ravich and Frolova (52) deals with the same subject. There has been much work in this field and the Russian studies are representative of the average.

E. Reaction with Esters

Vansheidt, Itenberg and Pazi (66) studied the preparation of methylene malonic ester from formaldehyde and malonic ester and investigated its polymerization to a colorless, thermoplastic resin. Well known techniques were followed and the results are not novel. A satisfactory process for preparing this material has not been published to date.

F. Reactions with Amines and Amides

Research in this field has been devoted principally to the preparation of urea-formaldehyde and melamine-formaldehyde resins. Petrov and co-workers have Russian patents covering the preparation of urea resins soluble in organic solvents (47) and the production of resin foams (48). Both involve carrying out the resin reaction at controlled, slightly acid pH values. The foam is made by beating the curing resin solution in the presence of a foaming agent. These procedures were patented in 1946-7 in Russia. The general procedures are similar to previous U.S. and English processes. Berlin and Iyumov (5) report the use of a phenol-formaldehyde-dicyanodiamide resin as a stabilizer for aqueous solutions of urea resins. Vaskevich and Reingach (69) made an interesting study of the hydrolysis of urea resins on heating with acid formaldehyde in 1948. Their work indicates that the decomposition process is a combination of colloidal

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peptization and chemical destruction. The kinetics of the urea-formaldehyde reaction were studied by Kveton and Kralova in 1952 (31).

Vansheidt and co-workers (67) studied the melamine-formaldehyde condensation in 1947 and established a relation between extent of condensation and flow of pressed resin powders. Preparation of molding powders with a cellulose filler is described. These results are not novel.

The preparation of the dimethylol derivatives of adipamide, sebacamide and suberamide by the standard alkali-catalyzed formaldehyde reaction was described by Arbuzov and Livshits in 1948. These derivatives should be interesting as resin intermediates.

G. Reactions with Hydrocarbons

The production of hydrocarbon resins and diaryl methanes by direct reaction with formaldehyde in the presence of strong sulfuric acid was apparently discovered by Nastyukov in 1903 (42, 43). A German patent by this inventor, dated 1929 (44) covers the use of this so-called "formolite" reaction for removing aromatics and hydro-aromatics from petroleum fractions. Prior to Nastyukov's work, Baeyer had shown in 1872 that methylene diacetate and methylal gave diaryl methanes and hydrocarbon resins on reacting with aromatics and concentrated sulfuric acid. In 1874, Grabowski (13) demonstrated the formation of dinaphthylmethane from naphthalene and methylal by this technique. In 1940, Moschinskaya and Globus (41) made a competent and detailed study of this reaction. Their findings indicate that methanol and traces of iron salts have a strong catalytic effect on the condensation.

Vororozhtzov and Yuruigina (72) published a study of the chloromethylation
of benzene by reaction with formaldehyde solution and hydrogen chloride in 1931.
Previous publications on the chloromethylation of aromatics describe the use
of formaldehyde polymers for this purpose. Since the latter are a more expensive
form of formaldehyde, the Russian work pointed to a more economical procedure.

The addition of chloromethyl ethers (ex formaldehyde-hydrogen chloride-
alcohol reactions) to butadiene was demonstrated by Pudovik and co-workers (50)
in 1949.

In 1948, Gorin and Charskaya (11) reported that significant amounts of
butadiene are formed by the reaction of formaldehyde and isopropyl alcohol.
The reaction can be carried out with methanol as a raw material in place of
formaldehyde by use of a mixed dehydrogenation - condensation catalyst
(mixed Lebedev catalyst). Earlier U.S. patents (1943-6) cover preparation
of butadiene from propylene and formaldehyde.

The earliest reported preparation of butynediol from formaldehyde and
acetylene is apparently Iocich's synthesis involving the reaction of formaldehyde
with the acetylene Grignard compound (73). In 1948, Gbertsiteli (10) described
the synthesis of vinyl-2-propynol from formaldehyde and vinyl acetylene presumably
by the Reppe reaction.

Russian research on the reaction of nitro-aliphatics and formaldehyde includes
Gorski and Makarov's demonstration that the methylolation of nitromethene is reversible
(12) and Malinowski and Urbanski's synthesis of hydropyrimidine deratives from
nitromethane, formaldehyde and ammonia (33).

H. Reactions with Heterocyclic Compounds

Chelintzov and Makarov (9) were apparently the first to demonstrate the formation of 2,5-dimethylolpyrroles by reaction of pyrrole and N-methyl pyrrole with alkaline formaldehyde solutions in 1916. In 1927, Potokhin (49) prepared N-methylol pyrrolidine, alpha-methylol pyrollidine and N-methylene bis-pyrrolidine by heating pyrollidine with alpha-polyoxymethylene. Schmidt and Petrov (54, 55) prepared pyridine-formaldehyde resins and patented their process in Russia in 1936. We know nothing concerning the possible utility of these resins.

V. HEXAMETHYLENETETRAMINE

As previously pointed out, Butlerov (8) was apparently the first chemist to prepare hexamethylenetetramine. This work was reported in 1859. In 1936, Kolosov (18) reported that 98% hexamethylenetetramine could be prepared by a gas phase reaction of formaldehyde and ammonia. To the best of our knowledge, a process of this type has never proved technically operable due to by-product formation. Klinov (17) has reported that chrome-and chrome-manganese steels as well cast iron containing 14.5% silicon are satisfactory for use in the manufacture of hexamethylene-tetramine.

Pushin and Zivadinovic (51) reported the preparation of a complex of phosgene and hexamethylenetetramine in a Yugo-Slav journal in 1936. Korostishev'ska (19) attempted to develop a method of hexamethylenetetramine analysis based on the formation of its tetra-iodo derivative without success.

A brief journal note by Karpukhin and Chetyrkin in 1944 describes current methods of manufacturing cyclo-trimethylene-trinitramine (RDX) with approx. 50% nitric acid and reports that up to 55% acid can be employed with proper cooling of the nitration mixture. However, it is stated that acid consumption is greater at the higher concentrations. This is far from representative of optimum processing techniques.

Al'vin-Gutzats and co-workers (1) covered the preparation of aromatic hydroxy-aldehydes by reaction of hexamethylenetetramine with a phenol in acid media in the presence of nitrosophenol, a nitroso-dialkylaniline or nitrobenzene sulfonic acid in 1946.

Borisek (6) described a method of differentiating various types of lignin by reaction with hexamethylenetetramine in 1951.

VI. FORMALDEHYDE ANALYSIS

Veksler (70, 71) has developed a spectrophotometric method for determining formaldehyde based on the use of Schiff's reagent. Soloveichik and Novikova (56) reported a simple procedure for hydrolyzing polyvinyl formals and determining the combined formaldehyde in these resins.

VII. MISCELLANEOUS

Minaev and Frolov (39) have reported the modification of cellulosic fabrics by treatment with formaldehyde gas and a solution of formaldehyde in acetone.

Borisek and Poloin studied the reaction of formaldehyde and lignin for differentiating various types of lignin (6).

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CONCENTRATION OF FORMALDEHYDE SOLUTIONS

Korzhev, P. P. and Rossinskaya, I. M.

CONCENTRATION OF FORMALDEHYDE SOLUTIONS

By: P. P. Korzhev and I M. Rossinskaya
Ref: J. Chem. Ind. (U.S.S.R.) 12 p. 610-14 (1935).

1. On The State of The Vapors of Formaldehyde Solutions.

The oxidation of hydrocarbons in many cases gives is one of the main products water solutions of formaldehyde of low concentration and various degrees of purity. In connection with our research in Soyuz on methods for the oxidation of hydrocarbons (methane, ethylene, etc.) the question arose of converting these dilute formaldehyde solutions obtained to commercial formalin, i.e., removal of impurities (chiefly acid) and concentration to 36-37% (formalin) or the solid form (paraformaldehyde).

Naturally it was at first decided to examine the possibility of fractional distillation as a means of obtaining satisfactory results.

The data in the literature do not give an answer to this question.

According to the data reported by Auerbach and Barschall (1), Wilkinson and Gibson (2), and others, fractional distillation under ordinary conditions is not a satisfactory method for concentrating formaldehyde solutions since the final distribution between distillate and residue is unfavorable.

On the other hand we have the information of Zimmerli (3) that by the careful fractionation of a 16% solution of formaldehyde containing methanol, he obtained in the first fractions methanol and in the following highly concentrated solutions of formaldehyde the content of which in individual fractions attained 55 gms. of formaldehyde per 100 cc. of solution. By this method practically all the formaldehyde distilled leaving almost nothing in the residue

Experiments were made to reproduce Zimmerli results in The Institute of Organic Catalysis. The separation was not effected (Korshev, P.P. and Florov, R.A.). However this did not disprove Zimmerli's data because we did not completely reproduce the conditions of the American investigator (A smaller column was used).

In any case it must be acknowledged that our information on the distillation of formaldehyde solutions is not very clear One of the reasons for this is the absence of sufficiently complete data on the partial pressure of formaldehyde vapors over the solution. (The new data of Ledbury and Blair/cover only the interval 0°-45°C.).

(4)

In connection with research on the working up of formalde-
hyde solutions obtained by oxidizing methane by the method of I. S.
Medvedev/we undertook the study of the constitution of the vapors
of formaldehyde solutions and the determination of the partial
pressure of the formaldehyde over a wide temperature interval.

Experimental Part

Apparatus

The determination of the vapor pressure of formaldehyde
was made by analysis of the constitution of the vapors of boiling
formaldehyde solution under various conditions of temperature and
pressure. This method proved very useful for the solution of the
practical problem before us.

In this work we made use of the apparatus of V. Kireev (6)
(see fig. I).

In reservoir 1 is placed the solution to be tested which
is heated to boiling. The vapor from the heated container passes
through tube 2 to the reflux condenser 3, condenses, and flows back
to the reservoir through tube 4. After the apparatus is completely
heated and the boiling becomes constant, stopcock 6 in tube 2 is
closed: whereupon the vapors are directed through the inner tube
5 into the condenser and thence into the reservoir 1. A small
sample of condensate is then collected in a graduated flask through
the 3-way stopcock 7. For determinations carried out at reduced
pressures a corresponding vacuum must be created in the flask in
which the sample is collected. The use of dephlegmators in the
apparatus leads to worthless values. Parallel experiments gave
satisfactory checks.

It is necessary to point out several difficiencies of
the apparatus. The tube with the ground-glass joint in which the
thermometer is suspended constitutes in itself a reflux condenser
and partially condenses the formaldehyde vapors.

Precipitation on the inner wall of drops of liquid makes
it extremely difficult to read the temperature. Furthermore fluid
condensing here slides down on the thermometer and hitting the
mercury bulb may cause low temperature readings.

Preparation of Formaldehyde Solution

Paraformaldehyde from the Kuskovsk Formaldehyde factory was taken as a raw material for this work. This product had a pasty consistency. The method of purification partly taken from the authors cited above consisted in first warming this paraform with a water bath under a reflux condenser at 60° for many hours. This operation removed all the easily volatile portions of the raw material. The residue polymerized quickly and was then heated to 50°-60° in the vacuum, after which it was depolymerized by heating to 110° to 115°C. catching the formaldehyde vapors in water. From this solution of formaldehyde, polymer was obtained again by vacuum distillation. The purified polymer was then vaporized and the formaldehyde gas dissolved in water. In this manner was obtained a solution containing 28 gms. of formaldehyde in 100 gms. of solution, from which solutions of other concentrations were obtained.

For carrying out comparative determinations we took a 16% pure formaldehyde solution prepared in an analogous process from a solid polymer of formaldehyde made by oxidation of methane.

The formaldehyde determinations were carried out by the iodimetric method of Romijn.

Results of Experiments

The objectives sought in our work were:

a) to explain the character of the relationship of the constitution of the vapors and partial vapor pressure of formaldehyde to the concentration of the solution.

b) to determine the relation of temperature to the partial pressure of formaldehyde for several concentrations.

From the results obtained from these experimental data may be calculated a series of other values to lay the foundation for this or other methods of studying solutions.

The results of the experiments are given in the tables and graphs.

In what follows we will make use of the designations shown below:

$C_{solution}$ = Concentration of formaldehyde in solution (in %)

C_{vapors} = Concentration of formaldehyde in vapor (in %)

P_{CH_2O} = partial pressure of formaldehyde in m.m. of mercury

P = normal pressure

t = boiling point of solution in degrees C (T-abs)

figure 2 is shown the relation of the concentration
of the vapor to the concentration of the solution at the boiling
point at the constant pressure of 750 mm. In order to do this
some of the figures are corrected for temperature.

An extremely important observation is the fact that
for low concentrations the content of the formaldehyde in the
vapor exceeds the concentration in the solution, (i.e. C_{vapor}

while as the concentration increases the inverse ration begins to
predominate. The transition point at which C_{vapor} equals $C_{solution}$
lies in the interval 9 to 12%.

Let us now look at the behaviour of solutions with an
initial concentration greater than 11 to 12%.

Since with solutions of this concentration the vapors are
poorer in formaldehyde than the initial solution $\left(\dfrac{C_{vapor}}{C_{solution}} \right)$

on distillation the distillate will possess a lower formaldehyde
concentration. Because of this there results an increase of concen-
tration of the solution in the distilling flask, provoking in turn
an increase in the second sample of analyzed distillate in comparison
with the previous test. This process continues until the end of
the distillation. As a result we have in the residue a concentrated
solution, and the distillate possesses an average concentration much
lower than the initial solution although individual final fractions
may exceed this value.

With solutions below 8-9% for which $\dfrac{C_{vapor}}{C_{solution}} >$

have an inverse picture of the distillation: the first fractions
contain more formaldehyde than the initial solution. In the distil-
lation process the residue is gradually impoverished in the distilling
flask.

This situation is well illustrated by the experiments of
Wilkinson and Gibson (see Fig. 3) which confirm us in our belief
that Auerbach was in error in his observation that the composition
of the vapors of formaldehyde solutions of all concentrations differ
from the initial solution in possessing a lower content of formalde-
hyde.

- 4 -

Determinations of relation of the partial pressure of formaldehyde vapor to temperature were carried out for three concentrations: the fluctuation of the concentration of the initial solutions in the range of 1% (for high concentrations) is not reflected in any observable alteration of the curve showing the constitution of the vapor. Accordingly we assign, for example the points obtained with solutions of 27.67, 28.24 and 28.62% to the average concentration, rounding it off to the whole number 28%. Consequently the other concentrations are also expressed in the approx. values 7% and 17%.

From the data shown in Table 2 and in Fig. 4, it may be seen that the results obtained with solutions of formaldehyde from various sources (from methane and from commercial formaldehyde) may be considered to be identical.

The relation of temperature to the partial pressure of formaldehyde in solutions of various concentrations may be expressed in the following form: $\log P_{CH_2O} = A - \dfrac{B}{T}$

P_{CH_2O} = pressure of formaldehyde vapor for a solution of a given concentration,

T = absolute temperature, A & B = constants

We fix B for all concentrations as equal to 3790. And A - as having the following values: for 28% solutions - 12.31, for 17% - 12.10 and for 7% - 11.75. Curves in Fig. 4 are constructed from this equation and show good agreement of the calculated data and the experimental.

Comparison of the data obtained by us with the anaglous data given by Ledbury & Blair shows that our data are lower than the values cited from their research measured in the range 0-45°C. The data of Ledbury and Blair agree well with the type empirical equation:

$$\log P_{CH_2O} = A - \dfrac{B}{T}$$

where B = 2905

Comparison of the equation of Ledbury and Blair and the equation set forth by us above shows that at high temperatures (85°-100°C.) the data of Ledbury and Blair must coincide with ours (assuming that the character of the relationship found by these authors is preserved for high temperatures).

For solution of these distillation questions the form of the isotherms for the total pressure of the vapor appears extremely important. The construction of these curves by proximate data from experiments is puzzling in consequence of the variation in boiling point of solutions, accordingly we had recourse to calculation.

As was shown above, the partial pressure of formaldehyde vapors follow sufficiently closely the formula:

$$\log P_{CH_2O} = A - \frac{2790}{T}$$

In an analogous manner, the vapor pressure of water over a formaldehyde solution may be expressed by the formula

$$\log P_{H_2O} = A' - \frac{2168}{T}$$

In Table 4 is given the comparison of the found values and those calculated by the empirical formulas.

The signification A and A' for other concentrations may be calculated from the data shown in Table 1 and further by means of graphic interpolations. By such a manner we obtain the following values (see Table 4).

Constructed on the basis of this calculation the isotherm (see Fig. 5) shows clearly a minimum vapor pressure for the concentration 11-12% corresponding however to the azeotropic mixture. This is in complete agreement with our experimental data. Here it should be observed that the isotherms for 97° and 98°C shown in Fig. 5 have the appearance of isotherms for higher temperatures. (Otherwise the curves would have to go down again at the length in order to approach the true value for the vapor pressure of pure water when $C_{solution} = 0$).

We already indicated the possible sources of error in the measured temperatures. This error increases still more in consequence of the approximations of the empirical formulas. That is why the cited isotherms reflect only the qualitative character of the distillation. In this they correspond to what we observe in reality on distillation of formaldehyde solutions. The introduction of corrections would not alter the form of the isotherms. At the same time they show that in the region of low conc. the boiling point of solutions is changed very insignificantly with concentration; the difference between the vapor pressure of water and that of the azeotropic mixture constitutes a value in the order of 10-15 mm. which corresponds to approx. 0.4° to 0.54° This explains why in our experiments we were unable to discover variations in boiling temp. of solutions with concentrations of 4.55 and 7.06%. This difference of temp. corresponds to the variation of pressure of 8 mm. which would not exceed a value of 0.3°C. and which could not be measured with certainty under the conditions of our experiments.

A very interesting peculiarity shown by formaldehyde solutions and already observed by Auerbach and noted by us is a deviation from the law of Konovalov. This is shown in the graphs in which the curve of condensate B in Fig. 5 goes higher than curve A while in ordinary cases the phenomenon takes place inversely. In other words: over solutions of formaldehyde we have vapor of such a composition that its boiling point is higher than the solution found in equilibrium with it.

Another expression of this anomaly is shown by the fact that with distillation of solutions with concentration greater than 12% the higher boiling component water is carried off preferentially and the mixture is enriched with the lower boiling component (if formaldehyde is considered as such) in conformity with which the boiling point of the residual mixture is reduced. With regard to solutions of lower concentration than 10%, there is a possibility of fractionally driving off completely all the formaldehyde with elevation of its conc. in the fraction while in normal cases for mixtures with partial pressure minima (e.g. HCl - H$_2$O) in the process of distillation the composition of the residual mixture approaches that of the constant-boiling mixture.

We think that the explanation of these anomalies should be sought in the phenomena of polymerization and depolymerization which take place during the concentration and distillation of formaldehyde solutions.

The system formaldehyde-water should be looked upon not as a binary mixture but as a solution in extreme measure of two forms of formaldehyde: the hydrated form methylene glycol and the polymeric form (CH$_2$O)$_n$, in equilibrium with each other.

With this very probable hypothesis, the term "lower-boiling" (with respect to water) component becomes vague: if we apply it with respect to the gaseous formaldehyde and, may be, to the hypothetical methylene glycol. To the polymer of formaldehyde the term is shown to be inapplicable. With this situation we have a marked deviation from the general laws for binary mixtures.

To distillation complicated by this picture may be added still another factor namely - time, which as it appears is required for the attainment of a condition of equilibrium between the stated forms.

On account of this, a recently concentrated solution of formaldehyde does not appear identical to an "older" conc. solution in which the polymerization process has proceeded further.

This is demonstrated experimentally by the study of the optical properties of formaldehyde (7) and the gradual disappearance of polymers after diluting those solutions.

We shall now apply our data to solution of the quest on of the optimum conditions for concentrating pure formaldehyde solutions.

With respect to distillation of atmospheric pressure the data obtained by us coincide completely with the observations of Wilkinson and Gibson permitting to sketch the same picture of distillation which was observed by these investigators in their work. The results of such distillation are not satisfactory for practical purposes. The much more favorable data obtained by Zimmerli are not explained by our results and require as it seems to us supplementary verification.

We have shown how the state of the vapor changes with lower temperatures.

From Table 2 it is seen that by decreasing the pressure at which the solution boils, the content of formaldehyde in the vapor falls rapidly.

As at 21 mm. and 20°-25°C, the state of the vapors in the solution with content 7, 17, and 28% CH_2O is expressed by the corresponding values 0.46%; 1.41% and 4.60%; thus when the pressure is almost atmospheric the corresponding values equal 6.95%, 18.0% and 22.8%.

Hence it follows that for concentration of pure formaldehyde solutions vacuum distillation may be successfully applied since one does not obtain highly concentrated distillate fractions and on distilling the water one obtains a concentrated formaldehyde solution in the residue.

The higher the vacuum the less the loss of formaldehyde in the form of weakly concentrated waste distillate.

For calculation may be used the above-stated empirical formula for the partial pressure of formaldehyde and water, subtracting one expression from the other we obtain

$$\text{Log } \frac{P_{CH_2O}}{P_{H_2O}} = A - A' - \frac{B}{T}$$

The values A and A' (for formaldehyde and water) may be taken from Table 4. For transition from the ratio of vapor pressures to conc. of distillate (in %) follow Table 5, composed by us on the foundation of the above cited experimental data.

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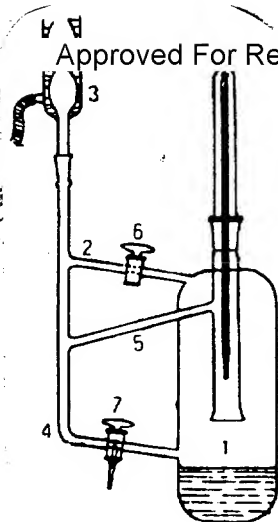
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Fig. 1

Table 1: State of Vapor as a Function of Concentration

$C_{соln.}$	$t°$	P	C_{vapor}	P_{CH_2O}	C корр.) Vapor Corr.)
4,55	99,0	735	5,09	23,4	18
4,71	99,0	753	5,20	24,6	--
7,06	98,5	735	8,34	39,0	45
7,03	98,8	753	9,08	43,6	--
11,74	98,5	753	11,34	54,4	--
17,34	97,5	735	16,98	81,1	17,17
17,50	98,5	753	17,27	85,1	--
19,51	98,5	753	17,99	88,9	--
19,54	97,5	735	17,98	87,2	18,19
25,90	97,5	735	22,36	109,5	22,63
25,90	98,5	753	22,73	114,5	--

Table 2: Variation of Partial Pressure of Formaldehyde with Temp. at Various Concentrations

BOILING POINT DATA

$C_{soln.}$	P	$t°$	C_{vapor}	P_{CH_2O}
6,82	21	19,5	0.46	0.06
6,82	104	51	1,81	1,16
6,82	201	65	2,63	3,27
6,82	300	75	3,82	7,0
6,82	400	82,5	4,31	10,9
6,82	608	93	5,96	23,4
6,82	740	98	6,95	32,3
7,05	21	19	0,77	0.04
7,05	82	46	1,36	0.68
7,05	206	66	2,67	3.35
7,05	503	88	4.77	15.2
16,86	21	21	1,41	0.18
16,86	20	20	1,19	0,14
16,86	102	51,5	4,73	3,06
16,86	308	75,8	7,27	14,0
16,86	400	82,0	10,70	27,2
16,86	506	87,0	11,31	36,3
16,86	603	92,5	15,15	59,1
16,86	701	96	15,4	69,7
17,34	200	66	5,74	7,1
17,34	306	75,8	9,58	18,5
17,34	402	82,0	10,40	25,5
17,34	508	88,0	11,86	38,3
17,34	742	98,1	14,96	71,9

Solutions of Form. obtd. by Oxidizing Methane

16,44	20	20	2,44	0.3
16,44	108	52	4,04	2,8
16,44	208	65	6,23	7,0
16,44	291	74	8,11	14,6
16,44	737	97,5	15,98	75,0
27,67	200	65,4	9,89	12,6
27,67	303	75,0	12,65	23,3
27,67	402	82,5	16,43	43,6
27,67	751	98,5	22,79	132
28,2	21	23,5	4,66	0,6
28,2	53	38,0	5,58	1,5
28,2	100	49,0	6,92	4,7
28,2	498	87,0	18,3	59,0
28,2	603	92,0	18,44	72,7
28,62	204	65,3	9,27	11,9
28,62	294	73,5	12,42	25,4
28,62	403	82,0	14,96	38,9
28,62	412	83,0	16,53	43,0

Note 1: The following graph (Fig. 2) makes use of these corrected values for the concn. of Form. in the vapors when the soln. is distilling at 753 mm. pressure.
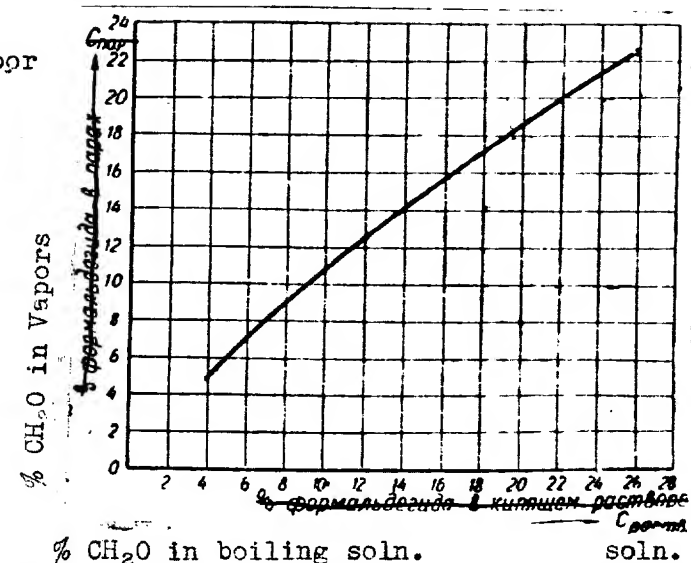

C_{vapor}
% CH_2O in Vapors
% CH_2O in boiling soln.

Fig. 2: State of Vapor as Function of Form. in soln. (Boiling Points at 753 mm.)

% CH_2O in Fraction (Gms/100 cc.)

Residue

An English copy of this should be in Wilkinson & Gibson's article. J.A.C.S. 43, 695 (1921)

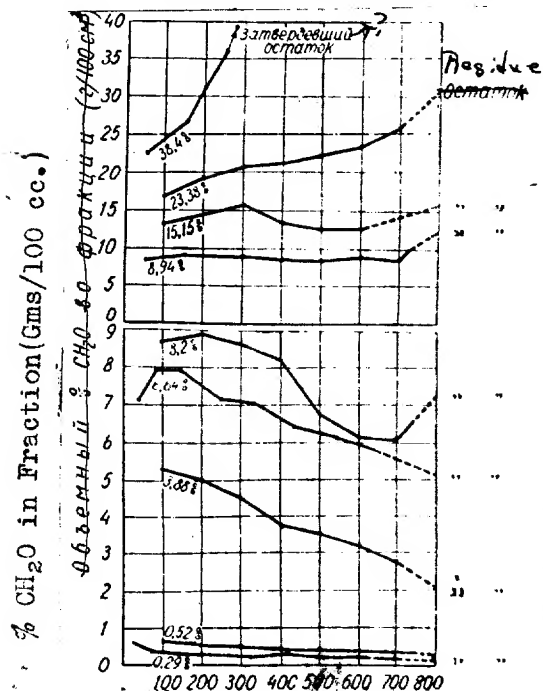Quantity of Distillate obtd. in cc.

Fig. 3: Chart of the distillation of Form. solns. of various concns. (according to Wilkinson & Gibson). Figures on curves indicate concn. of soln. distilled.

Fig. 4: Relation of Partial Press. of Form. Vapor to Temp. ver solns. of various concentrations.

Table: Comparison of ...... those Calculated from the Empirical Formula

t		C_{proz} %	Упруг. пар. P_{CH_2O} Found Найд.		Упруг. пар. воды P_{H_2O} Found Найд.				Примечание
				Calc. Выч.		Calc. Выч.	Found Найд.		
19,5		7	0,06	0,06	20,9	19,4	0,46	1,15	A = 11,75
51		7	1,16	1,07	102,8	101,5	0,81	75	
66		7	3,95	3,55	202,7	202	2,67		A' = 8,695
75		7	7,0	6,92	293	295	3,85	70	
88		7	15,2	17,0	488	495	4,77		
98		7	32,3	32,4	708	718	6,9	5	
20		17	0,14	0,15	19,9	19	1,19	25	
51		17	3,06	2,75	99	97	4,7	30	A = 12,10
76		17	14,0	(17,4)	294	291	7,2	9	
82		17	27,2	26,9	373	372	10,7	5	A' = 8,677
96		17	69,7	67,6	631	631	15,4	2	
98		17	71,9	77,6	670	682	14,9	6	
23,5		28	0,6	0,32	20,4	22,7	4,6	38	A = 12,30
38		28	1,48	1,29	51,5	50,2	5,5	10	
49		28	4,67	(3,5)	95	(87)	6,9	05	A' = 8,672
65		28	12,6	12,3	187	181	9,8	95	
82		28	43,6	42,7	358	366	16,4	9	
82		28	43,9	42,7	364	366	15,0	9	
87		28	59,0	58,9	439	446	18,3	4	
98,5		28	132	126	619	(673)	22,9	2	

Curves based on Equat:

$$\log P_{CH_2O} = A - \frac{3000}{T}$$

for
I A_I = 12,30
II A_II = 12,10
III A_III = 11,73

Table 4:

CONCENTRATION OF FORM. IN PER CENT

	5	6	7	9	10	11	12	15	17	20	25	28
FOR											2,26	12,30
A (для P_{CH_2O})	11,60	11,67	11,73	11,83	11,87	11,91	11,95	12,05	12,10	12,17		8,672
A (для P_{H_2O})	8,707	8,703	8,700	8,693	8,690	8,687	8,684	8,680	8,677	8,675	8,673	115
P_{CH_2O} при 97°	22,9	26,9	30,9	38,9	42,7	46,8	51,5	64,6	72,5	85,1	104,7	120
при 98°	24,0	28,2	32,4	41,5	44,7	49,0	53,7	67,6	75,9	89,1	110	649
P_{H_2O} при 97°	703	697	692	681	676	671	667	661	656	653	650	673
при 98°	729	723	718	707	701	697	692	686	681	678	675	
Average vapor press. P при 97°	726	724	723	720	719	718	718	726	729	738	755	764
То же при 98°	753	751	750	748	746	746	746	754	757	767	785	793
P(Same for	0,0305	0,0365	0,043	0,0560	0,0620	0,069	0,0755	0,0955	0,1095	0,13	0,1665	0,1890

Concentration of form. in moles (mole fraction)

Fig. 5: Character of the Isotherms for the total Pressure of CH_2O solns.

Table 5: Ratio of Vapor Press. and Conc. of Distillate in %

Ratio Отношение	$C_{пар}$ vapor	Ratio Отношение	$C_{пар}$ vapor
	−0,00	0,100	14,10
	1,65	0,110	15,30
	3,20	0,120	16,45
	4,70	0,130	17,60
	6,15	0,140	18,75
	7,55	0,150	19,90
	8,95	0,160	20,95
	10,30	0,170	21,95
	11,65	0,180	22,90
	12,95	0,190	23,90

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